

Electrochemical Growth of Linear Conducting Crystals in Microgravity

Raymond J. Cronise IV
Principal Investigator for Crystal
Growth Experiment GAS #608

PRESENTED AT THE FOURTH GET AWAY SPECIAL
EXPERIMENTER'S SYMPOSIUM
NASA GODDARD SPACE FLIGHT CENTER
OCTOBER 27-28, 1987

ABSTRACT

In recent years much attention has been given to the synthesis of linear conducting materials. These inorganic, organic, and polymeric materials have some very interesting electrical and optical properties, including low temperature superconductivity. The quest for methods to synthesize high-quality single crystals of these highly conducting materials has been a very important part of previous research. Because of the anisotropic nature of these compounds, impurities and defects will strongly influence the unique physical properties of such crystals. Investigations have demonstrated that electrochemical growth has provided the most reproducible and purest crystals thus far. Space, specifically microgravity, eliminates phenomena such as buoyancy driven convection, and could permit formation of crystals many times purer than the ones grown to date.

Several different linear conductors were flown on Get Away Special G-007 on board the Space Shuttle *Columbia*, STS 61-C, the first of a series of *Project Explorer* payloads. These compounds were grown by electrochemical methods, and the growth was monitored by photographs taken throughout the mission. Due to some thermal problems, however, no crystals of appreciable size were grown. The experimental results will be incorporated into improvements for the next two missions of *Project Explorer*, G-105 and G-608. The intent of this paper is to discuss the results and conclusions of the first mission, along with the modifications being made for the next two missions.

Introduction

Project Explorer's first mission contained three student experiments, including a Linear Conducting Crystal Growth experiment, and one experiment prepared by the Marshall Amateur Radio Club (MARC). Although all experiments operated as planned, the thermal environment was much colder than originally anticipated. The MARC experiment worked exceptionally well with 486 voice messages recovered out of 1440 transmitted. Upon examining the returned experiments, it was determined that Radish Seed Germination experiment suffered from the cold environment and early shutdown. The Crystal Growth experiment also suffered from the cold environment, however, valuable information was obtained. Due to the partial success of the Crystal Growth experiment, it then was considered for a reflight on a future *Project Explorer* GAS canister. This experiment will fly on both G-105 and G-608 missions.

Experiment

This experiment is being conducted to study the effects of microgravity on the growth of linear chain conductors. These conductors have the interesting property of anisotropy: their conductivity is different when measured along different directions in the solid. Two of the materials belong to one of the most studied groups of linear conducting solids, salts of tetracyanoplatinate (TCP). These salts were first prepared in 1842 by W. Knop, who noted that the salt had the color and sheen of bronze. It was not until 1964 that Klaus Krogmann of the University of Stuttgart determined a structure. The TCP group has the shape of a flat disk, but in the TCP salts prepared by Knop the disks are stacked like poker chips in many parallel columns. In the 1970's the properties of organometallic conductors were examined and this new research subbranch of solid state physics flourished. Part of the impetus for the study of linear chain solids was provided in 1964 by W. A. Little of Stanford University. He proposed that if a linear chain material could be designed to the correct specifications it might exhibit superconductivity not only at low temperatures, but also at room temperature.

The particular compounds which will be studied are: partially oxidized potassium tetracyanoplatinate (KCP), $K_{1.75}Pt(CN)_4 \cdot 1.5 H_2O$, and potassium tetracyanoplatinate bromide, $K_2Pt(CN)_4Br_{0.3} \cdot 3 H_2O$. These compounds both exhibit the columnar stacking typical of TCP complexes. Since the conductivity of a solid is determined by its electronic structure, this columnar stacking plays an important role in KCP electronic properties. In a highly conducting solid, orbitals of adjacent molecules and atoms overlap allowing electrons to readily move throughout the lattice. In the TCP complexes the platinum dz^2 orbitals extend above and below the TCP planes and allows for this overlap. In fact, the Pt-Pt separation (2.88 Å) is very close to the separation found in metallic platinum (2.79 Å). Overlap of the dz^2 electron orbitals gives rise to a band of electron states delocalized along the platinum chain. This overlap permits conduction along the molecular chain, but H. R. Zeller reported that the conductivity between columns is 100,000 times lower than along the chain.

The result of a material exhibiting such an ordered linear structure is the extreme susceptibility to defects and disorder. In a conventional metallic three-dimensional conductor, point defects can *reduce* conductivity by scattering electrons. These same point defects can cause *complete loss* of conductivity along the effected chain in a linear chain material, because electrons can no longer detour around the block. Arthur Epstein notes that a typical crystal ($1.00 \times 1.00 \times 0.01 \text{ mm}^3$) would contain approximately 1×10^8 parallel strands each of 3.5×10^6 collinear platinum atoms. Thus, purity levels (foreign impurities, end groups, and/or crystalline defects) of one part per million indicate that each stand averages more than three defects. These impurities could drastically alter the physical properties of the crystal, and most importantly, the electrical conductivity of the crystal.

In search of a synthesis that would lead to a defect free crystal, Arthur J. Epstein and Joel S. Miller devised the electrochemical techniques for preparing these crystals. When an electrical current is passed through a solution of potassium and tetracyanoplatinate ions,

partially oxidized KCP crystals form at the anode via electrochemical oxidation. KCP crystals grown in this way have room temperature conductivities 100,000 times greater than crystals prepared by more conventional means. If growing KCP crystals in the absence of gravity can produce crystals superior to the ones that have been grown to date, microgravity could become a valuable environment for pursuing this type of conductivity research and could ultimately lead to a better understanding of superconductivity.

Microgravity may offer several benefits to the electrochemical growth of these KCP complexes. In the early stage of their growth, KCP crystals form in a long, thin, needle-like structure, which thickens somewhat as the growth continues. In the initial growth period the crystals bend slightly due to their size and *weight*, placing a considerable amount of strain on the crystal lattice. In a low-gravity environment the lattice strain caused by this bending would be eliminated. Like any other solution crystal growth, the growing KCP crystal depletes the surrounding solution of solute as it grows. This depleted area has a lower density than the bulk solution and in a one gravity environment, it rises to the surface. It is this process that creates growth plumes which are characteristic of solution crystal growth. These growth plumes disturb the solution around the growing crystal and cause many microfluctuations at the crystal-solution interface. The elimination of such buoyancy driven convection may allow for the molecules to more properly align, which would result in a more ordered crystal.

These different factors will be investigated to determine if they play an important role in the quality of the crystals grown. The crystals grown in low-gravity will be directly compared with crystals grown on the ground for various physical and electrical properties.

Results From G-007

G-007 was launched on STS 61-C January 12, 1986 and landed January 18, 1986 with a mission elapsed time of 6 Days, 2 hours 4 minutes. Photographs were taken at two hour intervals to monitor the progress of the crystal growth, and they revealed a crippling problem. At 10 hours and 10 minutes (10:10) the growth solution froze thus stopping all KCP growth. The temperature had continually decreased from 5.6 °C at canister activation to -6.9 °C during this initial growth period. Figure 1 shows the cell before it had frozen and figure 2 is a photograph of the frozen cell. The solution remained solid for the next 8 hours. A subsequent photograph, taken at 28:10, showed that the solution had liquefied. Finally at 43:10, the first crystals appear on the anode (figure 3), after which the canister temperature once again dropped and the solution remained frozen for the rest of the mission. Figure 4 shows a summary of the growth chamber and canister temperature values. The chamber temperature followed very closely to the canister temperature, indicating that the thermal control system used was inadequate. After G-007 was returned, several very small crystals were recovered (sizes < 1mm), however, these crystals were much too small for any physical measurements.

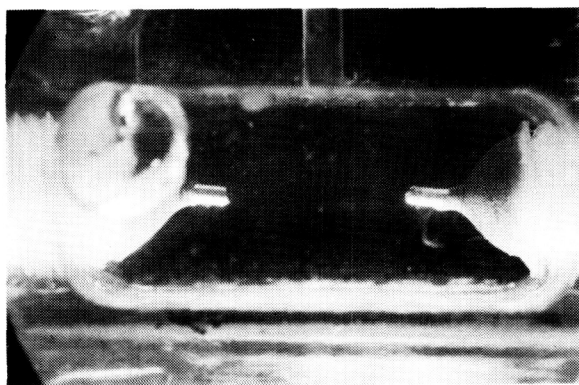


Figure 1

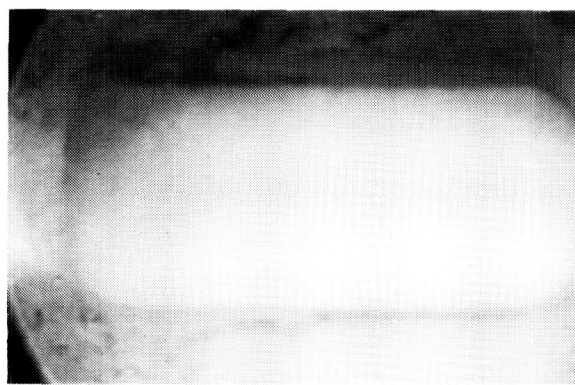


Figure 2

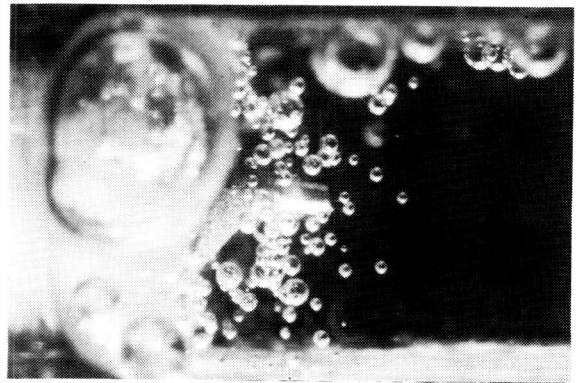
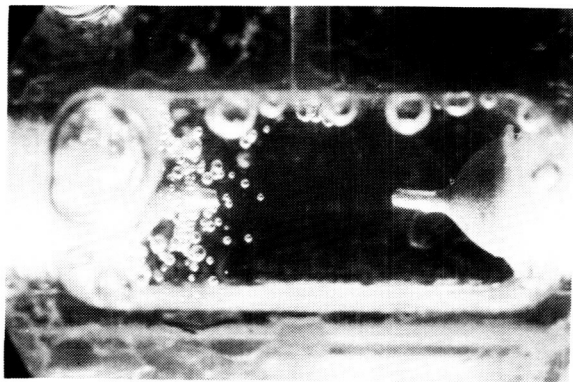


Figure 3

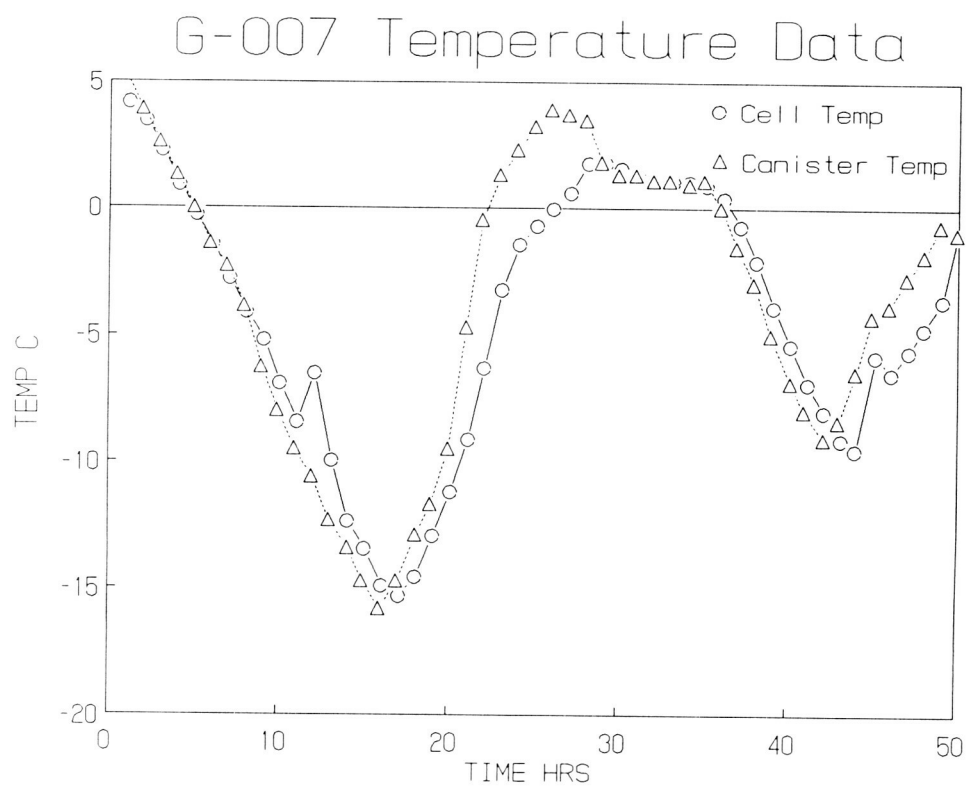


Figure 4

Modifications For G-105

G-105 was donated to the Consortium for Materials Development in Space at the University of Alabama in Huntsville (UAH), one of the nine Centers for Commercial Development of Space funded by NASA, for materials development experiments by faculty and students. Below is a summary of the experiments which will be included on G-105. Dr. Dwain Coble and Dr. Clyde Riley have agreed to allow one cell of linear conducting material to fly on their Electrodeposition experiment in G-105. The major components of the Electrodeposition experiment are shown in Figures 5 and 6. The experimental assembly will be mounted on an aluminum mounting plate which in turn is mounted to the GAS canister. The electrodeposition cells (Fig. 6) are stacked in two columns of four each. The cathode will be made of a thin sheet of platinum metal, while the anode will be modified to contain a small platinum stinger on which the crystals will grow.

Get Away Special G-105

Experiment 1	Separation of Aqueous Phases	Dr. Milton Harris
Experiment 2	Polymer Crystallization	Dr. Samuel McManus
Experiment 3	Monomer Crystallization	Dr. Milton Harris
Experiment 4	Electrodeposition and Co-Deposition	Dr. Dwain Coble Dr. Clyde Riley
Experiment 5	Cosmic Ray Determination	Dr. John C. Gregory

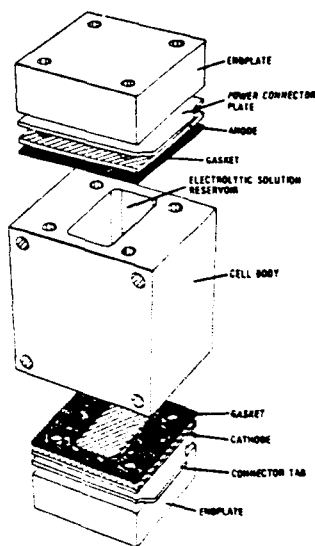


Figure 5

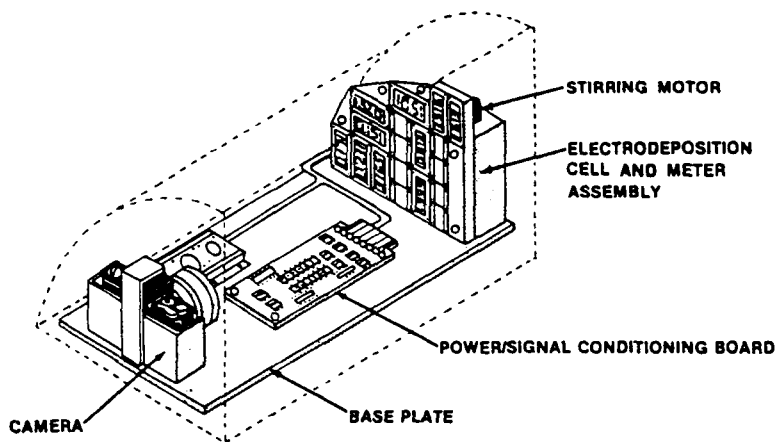


Figure 6

Modifications For G-608

The third *Explorer* payload is G-608 and contains only experiments proposed by students while attending *US Space Camp*. Below is a summary of the experiments which will be included on G-608.

Get Away Special G-608

Experiment 1	Insect Egg Growth	Bryan D. Agran
Experiment 2	Radish Seed Germination	Jay S. Andrews
Experiment 3	Yeast Growth	Greg T. Delory
Experiment 4	Bacterial Morphology	Tom P. Malone II
Experiment 5	Organometallic Crystal Growth	Raymond J. Cronise IV
Experiment 6	Silicon Crystal Growth	Seth Alain Watkins

The primary modifications for the crystal growth experiment will be in the thermal control system. Careful attention has been given to thermally isolate the growth chamber from the rest of the GAS package. The cells are attached to a glass cloth reinforced phenolic block which in turn is attached to the walls of the growth chamber. The growth chamber is then mounted to the experiment plate via two L-shaped support brackets that are also made of a glass reinforced phenolic material.

The Growth Chamber with three cells is shown in figure 7. Each cell will be fitted with a small thin film heater that will receive power from the canister SRB battery. The heaters will also be connected through a magnetic relay to a back-up dry cell power supply. This thermostatically controlled system will be activated during the shutdown procedures of G-608 to eliminate the possibility of freezing before the shuttle re-entry. The thermostat will be set at a minimum temperature to conserve the dry cell's power. This back-up thermal system in conjunction with the increased thermal isolation should provide the necessary improvements to the original G-007 flight hardware.

Growth Chamber



Figure 7

Conclusion

The first flight of this experiment on G-007 has given us a tremendous amount of valuable information to use for future *Explorer* flights. The most valuable information collected has been the thermal environment and SRB battery performance which were both monitored by the MARCE package. The SRB battery worked exceptionally well with more than 26 % reserve (See *MARCE Data Evaluation* by Edward F. Stluka in these proceedings). On the future flights, the SRB battery will be used as the primary power source and a dry cell battery pack will be used only for a backup. The importance of using all available methods of preventing thermal problems, has been a lesson learned by the *Project Explorer* team and other GAS experimenters. It is not always the best answer to just "use a bigger heater." Hopefully the increased thermal isolation in conjunction with better insulation, will eliminate future thermal difficulties.

Acknowledgment

The author would like to especially thank Mr. Konrad Dannenberg, Program Manager-*Project Explorer*, and the rest of the *Explorer* team for all of the effort, time, and support to make these student experiments possible. He also appreciates the funding provided by Dr. John A. Decaire of *Westinghouse Electric Corporation's Defense and Electronics Center* in Baltimore, MD. Finally, many thanks go to all who have helped from NASA/Marshall Space Flight Center, The University of Alabama in Huntsville (UAH), and The UAH Consortium for Materials Development in Space.

References

- Carneiro, K., Jacobsen, C. Williams, J., "Electrical Conductivities of Cation Deficient Analogues of KCP: $M_{1.75}Pt(CN)_4 \cdot 1.5 H_2O$, $M = K, Rb$," *Solid State Communications*, Vol. 31, 1971, pp. 837-841.
- Epstein, A., Miller, J., "Anomalous Electrical Conductivity of the Potassium Deficient Linear Chain Platinum Compound: $K_{1.75}Pt(CN)_4 \cdot 1.5 H_2O$," *Solid State Commun.*, Vol. 29, pp. 345-349.
- Epstein, A., Miller, J., "Linear-Chain Conductors," *Scientific American*, Vol. 241, No. 4 October 1979.
- Maybee, G.W., Riley, C., Coble, D.H., "Microgravity Effects on Electrodeposition of Metals and Metal-Cermet Mixtures," *1986 Get Away Special Experimenter's Symposium*, NASA CP-2438, 1986.
- Miller, J., "Electrochemical Syntheses of Partially Oxidized Platinum Complexes," *Inorganic Syntheses*, Vol. 19, No. 9, 1979, pp. 13-17.